Reversible Crosslinking in Cellulose. IV. Reactions of Tosylcellulose with Potassium Thiolacetate

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Synopsis

Reactions of tosylated cotton with potassium thiolacetate followed by alkaline hydrolysis yielded products containing both mercaptan and disulfide. The proportion of disulfide in the products depended much on the solvent used for the thiolacetylation. Reactions of tosylcellulose with thiolacetate in various solvents were investigated by polarographic and infrared analyses. Part of the acetylthio groups produced in acetone or in dimethylformamide was found to undergo rearrangement to form mercaptocellulose acetate. On the other hand, acetylthio groups formed in methanol were found to undergo complete methanolysis to form mercaptocellulose, and most of the mercapto groups thus produced were oxidized before hydrolysis treatment to yield the corresponding disulfide. This could account for the high disulfide proportion in the sample obtained through the reaction of tosylcellulose in methanol. Reaction of tosylcellulose with sodium thiosulfate yielded cellulose disulfide without mercaptan formation.

INTRODUCTION

Schwenker et al.[1,2] reported that mercaptocellulose was obtained by the reaction of tosylcellulose (TS) with potassium thiolacetate followed by alkaline hydrolysis. However, polarographic analysis of mercaptan (SH) and disulfide (SS) indicated that the alkaline hydrolysis product (M) contained a considerable amount of SS in addition to SH.[3] It was supposed that air oxidation of SH to SS took place during the alkaline hydrolysis procedure. The purpose of the present study is to clarify the mechanism of the SS formation.

EXPERIMENTAL

Materials and Reagents. All samples were prepared from 140 × 70 bleached, scoured, and unmercerized cotton printcloth kindly provided by Fuji Spinning Co. Ltd., Japan. Potassium thiolacetate was recrystallized from ethanol. Tosyl chloride was recrystallized from petroleum ether.

Tosylcellulose (TS). Cotton samples were treated with a 10% solution of tosyl chloride in pyridine with a liquor ratio of 1:30 at 70°C for a desired

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time, washed with a pyridine–water mixture, extracted with acetone in a Soxhlet apparatus, and dried in air. The sulfur contents of TS used in the present work were 1.26 (TS$_1$), 2.30 (TS$_2$), 2.60 (TS$_3$), 3.12 (TS$_4$), and 3.40 (TS$_5$).

Reaction of TS with Potassium Thiolacetate. TS was treated with potassium thiolacetate in acetone, dimethylformamide, or methanol with a liquor ratio of 1:100, washed with water, extracted with acetone, and dried in air. The product (AT) was hydrolyzed with 2% aqueous sodium hydroxide at room temperature for 1 hr to yield M.

Reaction of TS with Sodium Thiosulfate. TS was treated with 10% Na$_2$S$_2$O$_3$·5H$_2$O in ethanol–water (1:2 vol/vol) at 80°C, washed with water, extracted with acetone, and dried in air. The product was treated with 2% HCl at room temperature for 1 hr.

Iodine Oxidation of M. M was treated with iodine in a Clark-Lubs buffer (pH, 7.0) according to Schwenker et al.[1]

Oxidation of M with Hydrogen Peroxide. M was treated with 1% aqueous hydrogen peroxide with stirring at room temperature for 2 hr.

Analyses. SH and SS contents (both in μmoles/g) in modified cotton samples were determined by the polarographic method as reported previously.[3] Infrared spectra were obtained with a Shimazu IR 27-C spectrophotometer. KBr disks were made with the samples finely cut with scissors. Crystallinity indices were obtained by the method of Segal et al.[4] X-Ray diffractograms of the samples were recorded on a Rigaku Denki D-3F x-ray diffractometer with Cu K$_\alpha$.

RESULTS AND DISCUSSION

Potassium thiolacetate is sparingly soluble in acetone,[3,5] which Schwenker et al.[1,2] used for the treatment of tosylcellulose. In the previous papers,[3,6] good solvents such as dimethylformamide (DMF) and methanol were used for the thiolacetylation. Reexamination of the previous data suggested that the proportion of SS in M was much influenced by the solvent used for the reaction of TS with potassium thiolacetate. It became doubtful that the air oxidation of SH to SS occurred during the alkaline hydrolysis procedure, and a systematic study of the effect of the solvent was undertaken where the subsequent alkaline hydrolysis was carried out under the same conditions. In this paper, the proportion of SS is expressed by DS/MDS, which is defined as the ratio of the degree of substitution with SS to the degree of total substitution with SH and SS; it is calculated from the SH and SS contents (given in μmoles/g) by the equation

$$DS/MDS = 2(SS \text{ content})/\{SH \text{ content} + 2(SS \text{ content})\}.$$

The reaction product of TS with potassium thiolacetate is designated as AT, and its alkaline hydrolysis product, as M. The subscripts to AT and M distinguish the solvents used for the reaction of TS with thiolace-

tate, i.e., a, acetone; d, DMF; and m, methanol. The numerical subscript to AT and M indicates the parent TS sample used (see experimental section).

Table I shows that the DS/MDS of M_m is much higher than those of M_a and M_d. It was noted that the conversion of tosyl groups in acetone was about as high as that in DMF and in methanol, although potassium thiolacetate dissolved very slightly in acetone. The effect of the tosyl contents of TS on DS/MDS of M is given in Table II. The tosyl content had little effect on DS/MDS. The effect of the reaction period on DS/MDS was found to be very small (Table III). In these and other preparations done until now, DS/MDS ranges between 0.36 and 0.49 for M_a, 0.32 and 0.48 for M_d, and 0.70 and 0.81 for M_m.

TABLE I
Effect of Solvent in the Reaction of TS_2 with Potassium Thiolacetate

Reaction conditions		Hydrolysis product M			
Solvent	Time, hr	SH, μmoles/g	SS, μmoles/g	Tosyl conversion, %	DS/MDS
Acetone[a]	10	209	75	50	0.42
	50	242	107	63	0.47
DMF[b]	10	168	71	43	0.46
	50	207[d]	74	49	0.42
Methanol[c]	10	73	159	54	0.81
	50	98[e]	156	57	0.76

[a] Treated with saturated CH_3COSK in boiling acetone with excess solid CH_3COSK.
[b] Treated with 2.5% CH_3COSK at 75°C.
[c] Treated with 2.5% CH_3COSK in boiling methanol.
[d] SH estimated for the precursor AT_{d2}, 16 μmoles/g (see Fig. 1).
[e] SH estimated for the precursor AT_{m2}, 95 μmoles/g (see Fig. 1).

TABLE II
Reaction of TS of Different Tosyl Contents with Potassium Thiolacetate

Solvent used	TS used	Hydrolysis product M			
		SH, μmoles/g	SS, μmoles/g	Tosyl conversion, %	DS/MDS
Acetone[a]	TS_1	179	51	71	0.36
	TS_3	313	134	72	0.46
	TS_4	332	100	54	0.38
	TS_5	327	121	54	0.43
DMF[b]	TS_1	214	51	80	0.32
	TS_3	284	104	60	0.42
	TS_4	325	112	56	0.41
	TS_5	305	142	55	0.48

[a] Treated with saturated CH_3COSK in boiling acetone with excess solid CH_3COSK for 50 hr.
[b] Treated with 2.5% CH_3COSK at 75°C for 45 hr.

TABLE III
Treatment of TS with Potassium Thiolacetate for Different Periods

Reaction conditions		Hydrolysis product M			
Solvent used	Reaction time, hr	SH, μmoles/g	SS, μmoles/g	Tosyl conversion, %	DS/MDS
Acetone[a]	6	176 (176)[c]	60 (60)[c]	41	0.41
	10	209 (209)	75 (76)	50	0.42
	25	236 (232)	83 (90)	56	0.41
	50	242 (242)	107 (99)	63	0.47
	75	249 (246)	116 (119)	67	0.48
	100	260 (265)	120 (123)	69	0.48
DMF[b]	2	164	49	27	0.37
	5	209	74	37	0.41
	10	236	75	40	0.39
	20	277	103	50	0.43
	45	308	115	55	0.43

[a] TS_2 was treated with saturated CH_3COSK in boiling acetone with excess solid CH_3COSK.

[b] TS_4 was treated with 2.5% CH_3COSK at 75°C.

[c] Duplicate run where alkaline hydrolysis was carried out under nitrogen atmosphere.

The alkaline hydrolysis of AT_a was performed with carefully deaired aqueous sodium hydroxide under nitrogen atmosphere. The product was found to contain as much SS as that prepared under the usual hydrolysis conditions (see Table III). It was suggested that most of the SS was already formed during the preparation of AT, although the possibility of SS formation during storage of M should not be eliminated from consideration. The presence of SH and SS in AT_d was already mentioned in the previous paper[3] from the results of reactions of AT_d with CH_3HgI, both in neutral and alkaline (with Na_2SO_3) solutions at 30°C. Further analysis of the data (Fig. 6 in ref. 3) was made in this work. The extrapolation of the CH_3HgI consumption curve under neutral conditions to time zero (69 μmoles/g) was supposed to give the SH content in AT_d. The equilibrium uptake of CH_3HgI under alkaline conditions (457 μmoles/ g) was supposed to be equal to the sum of SH, SS, and acetylthio contents of AT_d, with the assumption that the acetylthio groups in the sample in the alkaline medium underwent complete hydrolysis to SH, which eventually reacted with CH_3HgI. The sum of SH and 2SS values of the corresponding M_d (549 μmoles/g) must be equal to the sum of twice the SS content and the SH and acetylthio contents of AT_d. From these relations, SS and acetylthio contents of AT_d are estimated, as shown in Table IV. The results indicate that 82% of SS in M_d was already present after the reaction of TS with thiolacetate in DMF. It is interesting to note that DS/MDS for AT_d was as high (0.73) as that of M_m.

The reactions of AT_d and AT_m with CH_3HgI under neutral conditions at a lower temperature (20°C) are compared in Figure 1. It was found
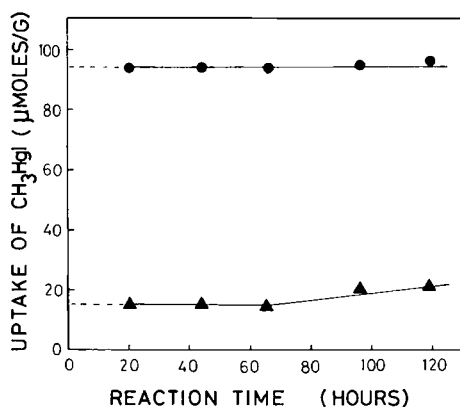
Fig. 1. Reaction of AT_2 with CH_3HgI in Sørensen buffer (pH, 7.2) at 20°C: (●) AT_{m2}; (▲) AT_{d2} (see Table I).

that hydrolysis of acetylthio groups at this temperature did not take place in an appreciable amount. It was significant that AT_m consumes as much CH_3HgI as the corresponding M_m. The maximum uptake of CH_3HgI of AT_m under alkaline conditions in the presence of Na_2SO_3 was measured, and the SH, SS, and acetylthio contents of AT_m were calculated (Table IV). It was found that AT_m contained only a negligible amount of acetylthio groups, and its composition was almost identical with that of the corresponding M_m.

In order to elucidate the mechanism of the formation of SH and SS during the treatment of TS with potassium thiolacetate, infrared spectra of AT were investigated (see Fig. 2). In addition to an absorption band at 1695 cm^{-1} (C=O stretching of thiolacetate[7]), AT_d showed an absorption band at 1740 cm^{-1}, indicating the presence of ester linkages. Both absorptions disappeared when the sample was hydrolyzed. The reaction of TS with potassium acetate in DMF yielded cellulose acetate, as evidenced with an infrared absorption at 1740 cm^{-1}. It is possible that the potassium thiolacetate used happened to contain potassium acetate. If TS was converted to acetate significantly with contaminated acetate, the tosyl and sulfur content should be decreased by the treatment. It was

TABLE IV
Estimation of SH and SS in AT[a]

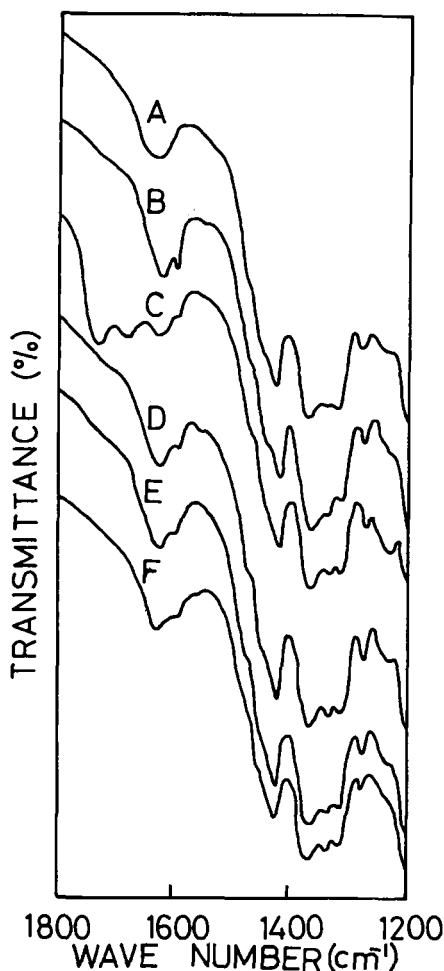| Solvent used	M		AT				
			CH$_3$HgI consumption		Estimated content		
	SH	SS	Neutral	Alkaline	SH	S	CH$_3$COS
DMF	352	112	69	457	69	92	296
Methanol	98	158	95	260	95	154	11

[a] All values are in μmoles/g.

Fig. 2. Infrared spectra of cellulose derivatives: (A) untreated cotton; (B) TS$_2$; (C) AT$_{d2}$; (D) M$_{d2}$; (E) AT$_{m2}$; (F) M$_{m2}$.

found that the infrared spectra of M showed absorption bands due to tosyl residues, and the loss in sulfur was very small (Table V). Adley and Owen[8] obtained a mixture of a thiolester and its rearrangement product, an O-acetate of 4-acetyl-5-deoxy-1,2-O-isopropylidene-5-mercapto-D-xylose, when 1,2-O-isopropylidene-5-O-tosyl-D-xylose was treated with potassium thiolacetate in boiling DMF. It was concluded that the re-arrangement of some of the acetylthio groups in cotton took place to yield mercaptocellulose acetate. This mechanism can explain both acetate and mercaptan formations during the treatment of tosylcellulose with potassium thiolacetate in DMF. The infrared spectrum of AT$_a$ was similar to that of AT$_d$, indicating the formation of mercaptocellulose acetate in acetone as well.

TABLE V
Sulfur Contents of M_d

TS	Sulfur content, %	
	M_d calcd[a]	M_d found
1.26	1.11	1.21
2.60	1.57	2.53
3.12	1.70	2.87
3.40	1.88	3.25

[a] Calculation based on SH and SS contents of M_d in Table II.

The infrared spectrum of AT_m did not show any absorption in the carbonyl region, in contrast to those of AT_a and AT_d. The absence of the thiolacetate group was already pointed out through the polarographic analysis. In this case, the thiolacetate formed underwent complete methanolysis during the treatment to form mercaptocellulose, and most SH further underwent oxidation to SS. Chapman and Owen[5] reported that the reaction of primary tosylates with potassium thiolacetate in ethanol produced thiolacetates and not mercaptans. That the reaction was carried out for comparatively short periods in their experiments may account for the difference of the type of products.

TS samples used in the present study were prepared by the reaction of cotton with tosyl chloride in pyridine for different periods. The crystallinity of TS and the corresponding M_d was measured according to the method of Segal et al.[4] The results are listed in Table VI. All the sample showed the cellulose I diffractions. The crystallinity of cellulose decreased slightly as the tosylation progressed. The thiolacetylation followed by alkaline hydrolysis did not alter the crystallinity of TS.

TABLE VI
X-Ray Crystallinity of Modified Cottons[a]

Sulfur in TS, %	Crystallinity index, %	
	TS	M_d
1.26	72	—
2.30	68	69
3.40	64	66

[a] Crystallinity index of untreated cotton, 75%.

The reaction of TS with sodium thiosulfate followed by acid hydrolysis was investigated for comparison with the reaction with thiolacetate. The results are summarized in Table VII. The reactivity of TS toward thiosulfate was much lower than that toward thiolacetate. It was significant that DS/MDS of the product was nearly equal to unity. Schwenker et al.[1] reported that the wet wrinkle recovery angle increased when tosylated cotton fabrics were treated with sodium thiosulfate and suggested that cellulose disulfide was produced by the treatment. The present work

confirmed the formation of cellulose disulfide through the reaction of tosylcellulose with thiosulfate. Comparison with the reaction with thiolacetate suggested that mercaptocellulose was not involved as an intermediate in the above disulfide formation. One of the two reaction mechanisms that Schwenker et al.[1] suggested for the disulfide formation required hydrogen ions. In one experiment, the effect of acid was examined to indicate that most of SS was formed before the acid treatment.

Oxidation of M with iodine was discussed in previous papers.[3,6] Some additional data are briefly given here. The iodine oxidation of M_a in

TABLE VII
Reaction of TS_2 with Sodium Thiosulfate

Reaction time, hr	SH, μmoles/g	SS, μmoles/g	Tosyl conversion, %	DS/MDS
10	3	14	4	0.90
25	3	28	8	0.95
50	5	49	14	0.95
75	7	67	20	0.95
100	11	76	23	0.93
150	9	87	25	0.95
150[a]	8	72	21	0.95

[a] Acid hydrolysis was omitted.

TABLE VIII
Iodine Oxidation of M_a

Sample	SH, μmoles/g before oxid.	SH, μmoles/g after oxid.	SS, μmoles/g before oxid.	SS, μmoles/g after oxid.	Iodine, consumed, μequiv/g	Δ(SH + 2SS),[a] μmoles/g	ΔI/Δ (SH + 2SS)[b]
M_{a1}	179	3	51	78	746	122	5.7
M_{a3}	313	8	134	161	1151	251	4.4
M_{a5}	327	11	121	169	1190	220	5.0

[a] Decrease in SH + 2SS through oxidation.
[b] Excess iodine consumed/decrease in SH + 2SS.

TABLE IX
Oxidation of M_d with Hydrogen Peroxide or Iodine[a]

Sample	Before oxid. SH	Before oxid. SS	After H_2O_2 oxid. SH	After H_2O_2 oxid. SS	After H_2O_2 oxid. (SH + 2SS)[b]	After I_2 oxid. SH	After I_2 oxid. SS	After I_2 oxid. (SH + 2SS)[b]
M_{d1}	206	52	114	73	50	3	76	155
M_{d3}	297	108	120[c]	128	137	9	137	230
M_{d5}	333	146	104	172	177	16	178	235

[a] All values are in μmoles/g.
[b] Decrease in SH + 2SS through oxidation.
[c] This sample was further oxidized with iodine and analyzed: SH, 9; SS, 120 μmoles/g.

water is summarized in Table VIII, which shows similar results to those in the oxidation of M_d.[3] Interestingly, the SS contents of samples (M_a and M_d) of lower DS/MDS increased appreciably by the oxidation. It was noted that no additional SS was formed when M_m of higher DS/MDS was oxidized with iodine.[6] Oxidation of M with hydrogen peroxide was compared with the iodine oxidation (Table IX). Both reagents gave about the same amounts of SS. These results seem to support the previously proposed mechanism of cellulose disulfide formation[6] that only a portion of mercapto groups in M are placed in proximity to each other and can be coupled to form disulfide groups and the rest of them remain unchanged or convert to some other group of higher oxidation states such as sulfonic acid groups, the amount of which corresponds to the decrease in the sum of the SH content and twice the SS content, depending on the oxidizing power of the reagent used. Hydrogen peroxide was found to be a weaker oxidizing agent, so that a considerable amount of the isolated mercapto groups remained unchanged. One of the samples treated with hydrogen peroxide was further oxidized with iodine. The SS content did not change, but the remaining SH disappeared by the iodine oxidation.

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